

Comparison of theoretical and experimental values of the number of metallic orbitals per atom in hypoelectronic and hyperelectronic metals

(saturation ferromagnetic moments)

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Contributed by Linus Pauling, August 8, 1985

ABSTRACT The statistical resonating-valence-bond theory of metals is applied in the purely theoretical calculation of the composition of the Ni-Cu alloy at the foot of the curve of saturation ferromagnetic moment, which marks the boundary between hypoelectronic and hyperelectronic metals and determines the value of the number of metallic orbitals per atom. The results, $\text{Ni}_{44}\text{Cu}_{56}$ and 0.722 metallic orbitals, agree with the observed values. This agreement provides strong support of the theory.

In 1938 it was pointed out that the physical properties of the transition metals indicate that the metallic valence is 6 in the sequence Cr to Ni and that the values of the saturation ferromagnetic moments show that only ≈ 8.3 of the 9 available $3d4s4p$ orbitals are used for occupancy by bonding electrons or ferromagnetic electrons (1). Later the apparently unused 0.7 orbital per atom was identified as required for unsynchronized resonance of covalent bonds (2), one such available orbital being needed for M^+ and M^0 and none for M^- . The amount of metallic orbital per atom was found (3) from the foot of the saturation ferromagnetic moment curve for the Co-Ni-Cu alloys, which occurs at about $\text{Ni}_{44}\text{Cu}_{56}$, to be ≈ 0.72 , corresponding to 28% M^+ , 44% M^0 , and 28% M^- .

Recently we have developed a detailed statistical theory of the unsynchronized resonance of covalent bonds for both hypoelectronic metals (4) and hyperelectronic metals (5). We now point out that this theory leads directly to a value of the amount of metallic orbital per atom and to the composition of the NiCu alloy that marks the division between hypoelectronic and hyperelectronic metals, and that these theoretical values are in excellent agreement with the empirical values.

For hypoelectronic metals the theoretical value (4) of ω , the amount of metallic orbital per atom, is

$$\omega = \frac{c + 1}{2c + 1} \quad [1]$$

with

$$c = \frac{1}{2} \left\{ \frac{v}{v + 1} + \frac{L - v}{L - v + 1} \right\} \quad [2]$$

Here L is the ligancy and v is the valence.

For hyperelectronic metals the theoretical value (5) of ω is found by solution of the simultaneous equations

$$x + 2y = 1 \quad [3]$$

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$$\frac{x}{2y} = \frac{(L - v)(z + 1)}{v(L - z)} \quad [4]$$

$$v = 2y(1 + z) + xz \quad [5]$$

$$\omega = \frac{1}{2}(x + 1). \quad [6]$$

Eq. 4 is equation 3 of ref. 5, z is the number of bonds formed by M^0 , $z + 1$ is the number of bonds formed by M^+ and by M^- , and M^+ , M^0 , and M^- occur in amounts y , x , and y , respectively.

These equations lead to the quadratic equation

$$(L - 2z - 1)x^2 - 2(z + 1)(L - z + 1)x + (z + 1)(L - z + 1) = 0, \quad [7]$$

which has the pertinent solution

$$x = e - \{e(e - 1)\}^{1/2} \quad [8]$$

with

$$e = \frac{(z + 1)(L - z - 1)}{L - 2z - 1} \quad [9]$$

and

$$v = z + 1 - x. \quad [10]$$

We now discuss the borderline composition $\text{Ni}_\alpha\text{Cu}_{1-\alpha}$. For Ni, with $L = 12$ and $v = 6$, the amount of metallic orbital is given as 0.6842 by Eqs. 1 and 2. For Cu, Eqs. 8 and 9 with $L = 12$ and $z = 5$ lead to $x = 0.5035$ and $v = 5.4965$, which with Eq. 6 give $\omega = 0.7518$, somewhat larger than the value for the hypoelectronic metal Ni.

We obtain the first equation for ω as a function of α by taking the weighted mean of the values of ω for Ni and Cu:

$$\omega = 0.6842\alpha + 0.7518(1 - \alpha). \quad [11]$$

A second equation is obtained by summing the orbitals. Of the 9 outer orbitals ($3d^54s4p^3$), 6 are used, with 6 electrons, in forming bonds. The alloy $\text{Ni}_\alpha\text{Cu}_{1-\alpha}$ has $11 - \alpha$ outer electrons, of which 6 are bonding electrons and $5 - \alpha$ occupy $2.5 - \alpha/2$ orbitals as unshared pairs. Hence $8.5 - \alpha/2$ orbitals are used for bonds or for occupancy by unshared electron pairs, leaving $0.5 + \alpha/2$ of the 9 available orbitals to serve as the metallic orbital:

$$\omega = 0.5 + \alpha/2. \quad [12]$$

The solution of the simultaneous Eqs. 11 and 12 leads to the values $\alpha = 0.444$ and $\omega = 0.722$, in complete agreement with the observed composition $\text{Ni}_{44}\text{Cu}_{56}$ and the corresponding value $\omega = 0.72$.

This agreement provides additional support for the resonating-valence-bond theory of metals and suggests that the ideas involved in this theory might be helpful in connection with the more conventional quantum mechanical treatments of the structure and properties of metals.

We thank the Japan Shipbuilding Industry Foundation (Tokyo) for partial support of this research.

1. Pauling, L. (1938) *Phys. Rev.* **54**, 899–904.
2. Pauling, L. (1949) *Proc. R. Soc. London Ser. A* **196**, 343–362.
3. Pauling, L. (1960) *The Nature of the Chemical Bond* (Cornell Univ. Press, Ithaca, NY), 3rd Ed., pp. 397–399.
4. Pauling, L. (1984) *J. Solid State Chem.* **54**, 297–307.
5. Kamb, B. & Pauling, L. (1985) *Proc. Natl. Acad. Sci. USA* **82**, 8284–8285.